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APPLICATION NUMBER: *60/496,777*
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Certified by

[signature] Jon W. Dudas

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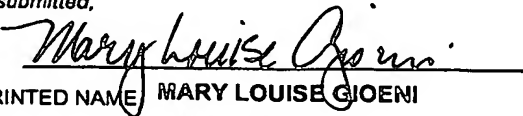Patent and Trademark Office

PROVISIONAL APPLICATION FOR PATENT COVER SHEET
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)

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[X] Additional inventors are being named on the ____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

NANOCOMPOSITES WITH CONTROLLED ELECTRICAL PROPERTIES

CORRESPONDENCE ADDRESS

Direct all correspondence to:

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[X] Firm or Individual Name	HESLIN ROTHENBERG FARLEY & MESITI P.C. C/O MARY LOUISE GIOENI
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ENCLOSED APPLICATION PARTS (check all that apply)

[X] Specification Number of Pages 44
[ ] Drawing(s) Number of Sheets
[ ] Application Data Sheet. See 37 CFR 1.76
[ ] CD(s), Number
[ ] Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)

[X] Applicant claims small entity status. See 37 CFR 1.27.
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
[X] No.
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Respectfully submitted,

SIGNATURE *Mary Louise Gioeni* Date 08/21/03

TYPED or PRINTED NAME MARY LOUISE GIOENI

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REGISTRATION NO. (if appropriate) 41,779
Docket Number: 0094.064P

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PROVISIONAL APPLICATION COVER SHEET
Additional Page

Docket Number	0094.064P	Type a plus sign (+) inside this box ⟶	+

INVENTOR(S)/APPLICANT(S)		
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Number __2__ of __2__

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CERTIFICATE OF MAILING BY "EXPRESS MAIL"

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Title: Nanocomposites with Controlled Electrical Properties

Docket No.:   0094.064P

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* Check in the amount of $80.00 for Prov. Appl Filing Fee
* Provisional Application for Patent Cover Sheet (2 pages) in duplicate
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NANOCOMPOSITES WITH CONTROLLED ELECTRICAL PROPERTIES

[0001] In the context of the present invention, 'nanoparticle' is defined as a particulate material having an average particle or grain size between 1 and 100 nanometers. Nanoparticles are distinguishable from particles having a particle size in the micron range, that is, greater than about 1 μm. Nanoparticles of any size, that is, ranging from about 1 nm to about 100 nm, may be used in the present invention. Particle size preferably ranges from about 10 nm to about 50 nm, and even more preferably from about 10 to about 30 nm.

[0002] Particle size distribution of the nanoparticles is typically narrow. A narrow particle size distribution is defined as one in which greater than 90% of the particles have a particle size in the range of 0.2 - 2 times the mean particle size. Preferably, greater than 95% of the particles have a particle size in this range, and more preferably greater than 99%. Another way to define a particle size distribution is in terms of the mean particle size and the width of the distribution; this method is used in the nanoparticle industry. The relationship between the width of the distribution curve at one half of the maximum value (full width-half max or FWHM) and mean particle size is used as a measure of broadness or narrowness of the distribution. For example, a distribution having a FWHM value that is greater than the mean particle size is considered relatively broad. Specifically, a narrow particle size distribution is defined in terms of FWHM as a distribution in which the FWHM of the distribution curve is equal to the difference between the mean particle size plus 40% of the mean and the mean minus 40% of the mean. (This may be simplified to two times 40% of the mean, or 80% of the mean. Using this simplified formula, the FWHM is less than or equal to 80% of the mean.) Preferably, the FWHM is less than or equal to the difference between the mean plus 30% and the mean minus 30% (60% of the mean.) More preferably, the FWHM is less than or equal to the difference between the mean plus 20% and the mean minus 20% (40% of the mean).

[0003] Nanoparticles useful in the present invention may be equiaxed, such that their shape is quasi-spherical. The long axis of a particle is defined as the longest axis

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through a particle, and the short axis means the shortest axis through a particle. The long axis of the nanoparticles for use in the present invention is approximately equal to the short axis, resulting in a particle shape which is quasi-spherical. In this case, for at least 90% of the nanoparticles, the ratio of the length of the short axis to that of the long axis is at least 0.1, preferably 0.4, and more preferably 0.8.

[0004] Non-spherical nanoparticles may also be used in the present invention. For example, nanotubes having an average particle diameter of approximately 1-100 nm may be used. Nanotubes have a very high aspect ratio, that is, ratio of length to diameter, typically ranging from 25 to 1,000,000. Nanoparticles that are not nanotubes or equiaxed and having an aspect ratio between 1 and 25 may also be used.

[0005] Further, the surface of a nanoparticle utilized in the present invention is typically chemically clean, that is, uncontaminated by residues from chemicals used in the synthetic process. Methods that produce nanoparticles from a gas phase, such as a gas condensation process, such as that described in U.S. Patents 5,128,081 and 5,320,800, the contents of which are incorporated herein by reference, typically yield a clean surface. Nanoparticles made by wet chemical methods are often contaminated by residues from chemicals used in the process; these particles may be subject to a post-production clean-up process to yield a chemically clean surface. For example, many processes for the production of titanium dioxide particles involve the oxidation of $TiCl_4$ to TiO_2. The surface of particles produced by this process contains residual chloride ions from the $TICl_4$. These residues may be removed by chemical cleaning processes, if desired. Nanoparticles produced by a gas condensation process are not contaminated by process residues, because no solvents, reagents or intermediates are used. Therefore, zinc or titanium dioxide nanoparticles for use in the present invention are preferably prepared by a gas condensation process.

[0006] A gas condensation process for the preparation of nanoparticles typically involves evaporation of a metal precursor material from which the nanoparticles will be synthesized at gas pressures of less than one or equal to one atmosphere. The evaporated metal condenses into small particles in the gas atmosphere and the

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resulting nanoparticles are collected on a surface within the reactor. Any metal or metal compound capable of being volatilized may be used in this process. Exemplary metals are titanium, copper, silver, gold, platinum, and palladium. The metal nanoparticles may be further subjected to a reactive gas atmosphere to form oxides, nitrides, carbides, sulfides, fluorides, and chlorides. Exemplary metal oxide nanoparticles are those composed of aluminum oxide, antimony tin oxide, cerium oxide, copper oxide, indium oxide, indium tin oxide, iron oxide, tin oxide, titanium dioxide, yttrium oxide, zinc oxide, barium oxide, calcium oxide, chromium oxide, magnesium oxide, manganese oxide, molybdenum oxide, neodymium oxide, and strontium oxide. Metal titanate and metal silicate nanoparticles including, for example, strontium titanate, barium titanate, barium strontium titanate, and zirconium silicate may also be used. Zinc oxide nanoparticles of varying particle size, synthesized by a gas condensation process, are commercially available from Nanophase Technologies Corporationalong with many of the nanoparticles listed above.

[0007]   Nanoparticles used in the present invention may be crystalline materials, and referred to as nanocrystalline. Each nanocrystalline particle is composed of a single grain, that is, a single crystal consisting of atoms arranged in an orderly pattern. Nanocrystalline materials have grains containing thousands to tens-of thousands of atoms as compared to millions or trillions of atoms in the grains of conventional particles, and have a significantly higher percentage of atoms present on the surface of the particle.

CLAIMS

1.   A nanocomposite comprising a dispersion of a nanoparticle filler in an electrically insulating polymer.

2.   A nanocomposite according to claim 1, wherein the nanoparticle filler comprises a semiconductor.

3.   A nanocomposite according to claim 1, wherein the nanoparticle filler comprises a conductor.

4.   A nanocomposite according to claim 1, wherein the nanoparticle filler comprises a metal oxide.

5.   A nanocomposite according to claim 1, wherein the nanoparticle filler comprises zinc oxide.

6.   A nanocomposite according to claim 1, wherein the nanoparticle filler comprises titanium dioxide.

7.   A nanocomposite according to any of the above claims, wherein the polymer comprises a thermoplastic polymer.

8.   A nanocomposite according to any of the above claims, wherein the polymer comprises polyethylene.

9.   A nanocomposite according to any of the above claims, wherein the nanoparticle filler is surface-modified by treatment with a silane coupling agent.

10.   A nanocomposite according to any of the above claims, wherein the nanoparticle filler is surface-modified by attachment of one or more organic groups thereto.

11. A nanocomposite according to claim 9 or 10, wherein the surface of the nanoparticle filler comprises an organic group is selected from alkyl, alkylamino, amino and carboxy.

12. A nanocomposite according to claim 11, wherein the organic group is selected from methyl, vinyl octyl, aminopropyl and acetoxy.

13. A nanocomposite according to any of the above claims, wherein the dispersion is inhomogeneous.

14. A nanocomposite according to any of the above claims, wherein the nanoparticle filler comprises a range of particle sizes.

15. A nanocomposite according to any of the above claims, additionally comprising at least one filler having a particle size in the micron range.

16. A nanocomposite according to any of the above claims, wherein the dispersion is derived from a blend of said nanoparticles and particles of said polymer having a particle size in the micron range.

CONTROLLED RESISTIVITY AND PERMITTIVITY: ZINC OXIDE

17. A nanocomposite having controlled resisitivity and permittivity, said nanocomposite comprising a dispersion of a nanoparticle filler capable of electrical conduction between particles in an electrically insulating polymer.

18. A nanocomposite according to claim 17, wherein electrical resistivity of the nanocomposite as a function of applied field strength is nonlinear

19. A nanocomposite according to claim 17, wherein the nanoparticle filler comprises a semiconductor.

20. A nanocomposite according to claim 17, wherein the nanoparticle filler comprises a conductor.

21.   A nanocomposite according to claim 17, wherein the nanoparticle filler comprises a metal oxide.

22.   A nanocomposite according to claim 17, wherein the nanoparticle filler comprises zinc oxide.

23.   A nanocomposite according to any of claims 17-22, wherein the polymer comprises a thermoplastic polymer.

24.   A nanocomposite according to any of claims 17-22, wherein the polymer comprises polyethylene.

25.   A nanocomposite according to any of claims 17-24, wherein the nanoparticle filler is surface-modified by treatment with a silane coupling agent.

26.   A nanocomposite according to any of claims 17-24, wherein the nanoparticle filler is surface-modified by attachment of one or more organic groups thereto.

27.   A nanocomposite according to any of claims 17-24, wherein the surface of the nanoparticle filler comprises an organic group is selected from alkyl, alkylamino, amino and carboxy.

28.   A nanocomposite according to any of claims 17-24, wherein the organic group is selected from methyl, octyl, vinyl, aminopropyl and acetoxy.

29.   A nanocomposite according to any of claims 17-28, wherein the dispersion is inhomogeneous.

30.   A nanocomposite according to any of claims 17-29, wherein the nanoparticle filler comprises a range of particle sizes.

31.   A nanocomposite according to any of claims 17-30, additionally comprising at least one filler having a particle size in the micron range.

32.   A nanocomposite according to any of claims 17-31, wherein the dispersion is derived from a blend of said nanoparticles and particles of said polymer having a particle size in the micron range.

IMPROVED BREAKDOWN STRENGTH: TITANIUM DIOXIDE

33.   A nanocomposite having high breakdown strength comprising a dispersion of a nanoparticle filler in an electrically insulating polymer.

34.   A nanocomposite according to claim 33, wherein the nanoparticle filler comprises a semiconductor.

35.   A nanocomposite according to claim 33, wherein the nanoparticle filler comprises a conductor.

36.   A nanocomposite according to any of claims 33-35 wherein the nanoparticle. filler comprises a metal oxide.

37.   A nanocomposite according to any of claims 33-35 wherein the nanoparticle filler comprises titanium dioxide.

38.   A nanocomposite according to any of claims 33-37, wherein the nanoparticle filler is surface-modified by treatment with a silane coupling agent.

39.   A nanocomposite according to any of claims 33-37, wherein the nanoparticle filler is surface-modified by attachment of one or more organic groups thereto.

40.   A nanocomposite according to any of claims 33-39, wherein the surface of the nanoparticle filler comprises at least one hydrophobic group.

41.   A nanocomposite according to claim 40, wherein said at least one hydrophobic group is alkyl.

42.   A nanocomposite according to claim 40, wherein said at least one hydrophobic group is decyl.

43.   A nanocomposite according to any of claims 33-40, wherein the surface of the nanoparticle filler comprises an alkylamino group.

44.   A nanocomposite according to any of claims 33-43, wherein the polymer comprises a thermoplastic polymer.

45.   A nanocomposite according to any of claims 33-43, wherein the polymer comprises polyethylene.

METHOD CLAIMS

46.   A method for modulating electrical properties of an electrically insulating polymer, said method comprising preparing a nanocomposite according to any of the above claims.

47.   A method according to claim 46, wherein said electrical properties are selected from resistivity, permittivity, electrical breakdown strength and combinations thereof.

INVENTION DISCLOSURE

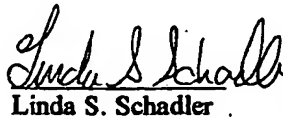## Nan c mposite with C ntroll d Resistivity and P rmittivity

Polymers have been used for a long time for electrical insulation. For example, low-density polyethylene (LDPE) has good electrical insulating properties such as high resistivity and low permittivity. These properties can be modified by introducing inorganic filler particles of various sizes down to the nanometer (nm) scale. The filler content and dispersion state can also be used to control properties. These filler particles have been typically in the micrometer (μm) size scale. The recent availability of nanoparticles has made it possible to fabricate composites with a controllable combination of useful properties that was previously impossible. For an initial example of this control, ZnO nanoparticles were mixed with LDPE to obtain nanocomposites with controlled dispersion state resulting in modified resistivity and permittivity.
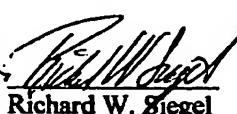
It has been found that changes in resistivity and permittivity can be controlled by changing the distribution state of the filler particles. Control of the dispersion state was achieved by mixing the composite using a combination of mixing methods and by varying the mixing time. Uniform distribution of the filler particles was obtained by melt mixing and highly nonuniform distribution was obtained by ball milling polymer powder and nanoparticles. More control can be achieved by varying the size of polymer powder and nanoparticles. The percolation limit (defined as the concentration above which the resistivity of the composite decreases) changed from 14 to approximately 1 vol.% depending on the distribution of the filler. The percolation limit is also sensitive to the filler particle shape. Above the percolation limit, the resistivity of the nanocomposite decreases exponentially, but the rate of decrease for well-dispersed composite is much lower than that of an inhomogeneously dispersed composite.

By changing the chemistry of the interface, we are also able to affect the change of resistivity and permittivity with filler content. The effect is significantly larger than with conventional micron size fillers due to the high surface area of nanoparticles. A change in permittivity was observed for composites filled with surface modified nanoparticles. On the other hand, the permittivity of the nanocomposite without filler surface modification remains the same as that of the conventional composite at a given filler concentration. Regardless of filler particle size, the permittivity is proportional to the volume content of the filler. Another advantage of filler surface modification is the ability to achieve high permittivity values without increasing loss. By combining these properties, a nanocomposite with desired resistivity and permittivity can be made using nanoparticles. This is a rather general phenomenon applicable to a wide range of nanocomposite material combinations.
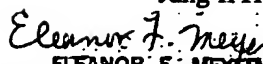
The change in resistivity and permittivity depends on the physical properties of the ZnO nanoparticles (with and without surface coating) and their distribution in the polymer matrix, but not on the properties of the LDPE matrix. Therefore, the same behavior is expected when ZnO nanoparticles are mixed with other polymers. Also, other nanoparticle fillers that have similar electrical characteristics to those of ZnO nanoparticles that allow electrical conduction between particles via a tunneling mechanism would offer the same capabilities. Through control of resistivity and permittivity, such nanocomposites can be used for components in the field of electrical transmission and distribution, electrical machines, and in microelectronic dielectric components.

Jung-Il Hong   Linda S. Schadler .   Richard W. Siegel   Eva Mårtensson

Rensselaer Polytechnic Institute

Office of Technology Commercialization

Invention Disclosure Record

RPI Case Assignment

OTC Official

Instructions

Type or print all answers to questions. Be as detailed as possible Use numerals to identify parts correspondinly designated in the drawings. Drawings should illustrate the invnetion in the environments in which it would be used. The drawings and description should emphasis any new structural or arrangement features of the invnetion. Use additional sheets to elagborate, or attach descriptive materials. Each additional sheet and drawing of th description shall also be signed and dated by the inventor(s). Upon completion return to the <u>Office of Technology Commercialization,</u> Incubator Center, JBldg 3208, Troy, New York 12180, or call (518) 276-6023 with questions.

Date Jan. 28, 2003

1. As required under part 2 of the Institute's Intellectual Property Policy approved by the Board of Trustees on May 21, 1988, I am enclosing a disclosure of Invention titled:

   Nanocomposites with Controlled Resistivity and Permittivity

2. Name of Inventor(s), Address, and Citizenship

   Jung-Il Hong; 285 Sunset Ter., Troy, NY 12180; Citizenship: Korea
   Linda S. Schadler;
   Richard W. Siegel;
   Eva Mårtensson;

3. List dates for the following:
Invention conceived by inventor(s): Feb. 12, 2002
First sketch of invention prepared
First written description prepared: Feb. 25, 2002
First model or full size device completed Feb. 25, 2002
First test or operation of invention: Apr. 8, 2002

First offer of sale
First sale
First public disclosure

4. The invention was made under one or more of the following circumstances:
███

b) In connection with any agreement of any type which gives or may give any party
rights whatsoever in the invention
If so, please identify the agreement and, if possible, attach a copy.
c) On my own time as follows:
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b) Other (describe)
c) Use of Institute time, materials, or facilities(describe:
d) In connection with Institute Activities:

This project was completed in the Rensselaer Nanotechnology Center under the Industrial
Partnership program. Thus the invention is jointly owned by RPI and ABB (See Chuck
Rancourt for details if needed)

5. List names of each person (other than co-inventors) who have knowledge of the
invention.

Thomas Liljenberg, Carina Önneby

6. List any publication, oral presentation or offer for sale that has been made which
included this invention.

7. List pertinent pending patent applications. Publication and reports (e.g. Research.
reports, service problems, etc) which contain information bearing the problem to be
solved by the invention or on the invention itself.

Research reports to ABB from RPI.

8. Prior Art as known by the inventor - A summary

Incorporation of oxide nanoparticles rather than conventional micron size particles into
the insulating polymers decrease the percolation limit as determined by electrical
conduction (patent in progress). There also have been attempts to change the electrical
properties of polymer-based material by filling the matrix with conducting material such
as carbon black. But, in this work, we try to control the electrical properties of polymer
composite by changing the spatial distribution and surface chemistry of the nano-sized
filler materials.

Electrical Behavior of Low Density Polyethylene Containing an Inhomogeneous Distribution of ZnO Nanoparticles

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(Last edited on January 26, 2003)

Abstract

ZnO nanoparticles were mixed with low density polyethylene (LDPE) to form nanocomposites. The distribution of ZnO filler particles was controlled by changing the mixing method, and the effects of inhomogeneous distribution on the electrical resistivity were measured. The percolation limit in the composites with inhomogeneous filler distribution decreased significantly compared to that of the analogous nanocomposite with uniform filler distribution, and the resistivity of the filled composites decreased as a function of applied field strength, exhibiting a nonlinear I-V relationship. The nonlinearity increased with ZnO filler concentration.

Introduction

Polymer nanocomposites have been shown to have many advantageous properties primarily due to the small size and large surface area of the nanofillers (fillers with at least one dimension less than 100 nm).[1,2] The small filler size leads to electrical, optical, and mechanical properties different from those of bulk materials[2,3], and acts as a smaller defect than traditional fillers preventing early electrical and mechanical failure. For example, Henk *et al.*[4] reported increased electrical discharge endurance with silica nanoparticles in epoxy resin. Ash *et al.*[5,6] found a significant increase in ductility and a decrease in glass transition temperature for PMMA filled with alumina nanoparticles.

The changes in the properties caused by the introduction of nanoparticle fillers are strongly controlled by the dispersion state of the filler particles in the polymer matrix. Achieving a good dispersion of the fillers has been one of the major issues in the processing of polymer nanocomposites. Agglomeration frequently leads to loss of some improvements in properties attained by employing nanoparticles as fillers.[7] While good dispersion it critical, it is not always apparent that the distribution of fillers needs to be uniform throughout the matrix for the best results. Well dispersed, but non-uniformly distributed, filler particles may lead to optimized properties. In this paper, we show that it is possible to achieve improved electrical properties by means of an inhomogeneous filler distribution.

Another advantage of nanofillers is that percolation can be achieved at lower volume fractions.[8] Electrical properties of nanoparticle filled polymers change significantly at percolation.[9] The resistivity of the composite drops abruptly as the filler volume fraction increases above the percolation limit. Because of the cost of fillers and the possible degradation they may cause in other properties,[10] there is interest in decreasing the volume fraction of filler. We have shown previously that the percolation limit of composites with uniform filler distribution changes as the size of filler particles decreases.[8] The percolation limit also decreases when the filler particles have a high aspect ratio like a carbon nanotube.[11] Further decrease of the percolation limit by creating mixed regions of high and low filler concentration due to an inhomogeneous filler distribution is demonstrated in the present work. A lower percolation limit due to inhomogeneous distribution of carbon black particles in a polymer matrix was recently

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reported by Wycisk et al.[12] While carbon black is typically used to decrease the resistivity of composites, in the present work, ZnO semiconductor particles were introduced to make composites with resistivity values between those of conductors and insulators. Resistivity values of such a magnitude are required for field grading materials used in high voltage cable accessories. The nonlinear electrical behavior of ZnO[13] is also important for these field grading materials.

Experimental

ZnO nanoparticles were donated by Nanophase Technologies Corporation, and the average particle size was determined to be approximately 50 nm from TEM observation. For uniform distribution of filler particles, the nanoparticles were melt-mixed with low density polyethylene (LDPE; DOW 681I) pellets using a torque rheometer (Haake batch mixer system 90) as described in Ref. 14. The resulting composite was then examined with field-emission scanning electron microscope (FESEM, JEOL JSM-6335F), and fillers were observed to be well dispersed and distributed uniformly in the polymer matrix. Non-uniform distribution of the filler in the matrix was achieved by ball milling the nanoparticles with micron-size LDPE powders obtained from Ultra Chemical Inc. The mixture of particles was ball milled at room temperature for 24 hours so that ZnO nanoparticles were embedded in the soft surface of the LDPE particles. Neither the LDPE powders nor the ZnO nanoparticles were observed to break into smaller pieces during the ball milling. Together they formed large agglomerates approximately 1 mm in diameter composed of many LDPE powder particles coated with ZnO nanoparticles. The mixtures were then hot pressed at approximately 170°C to form a disc-shaped specimen with a diameter of 7.5 cm and a thickness of approximately 0.03 cm. The microstructure of the composites with inhomogeneous filler distribution was examined with FESEM, and the electrical resistivity was measured under an applied electrical field of 10 kV/cm over the thickness of the disc specimens with a guard ring to remove any effect of surface conduction.[15]

Results

The specimens were broken in liquid nitrogen and their fracture surfaces were examined by FESEM. The homogeneous and inhomogeneous distributions of filler particles are shown in Fig. 1(a) and 1(b), respectively. The polymer matrix is mechanically stronger than the filler aggregates and the composite breaks primarily through the filler aggregates. Therefore, filler nanoparticles were exposed on the fracture surface of the composites. They appear as aggregated particle lumps in Fig. 1(b), while the particles in Fig. 1(a) are well separated from one another. ZnO nanoparticles were embedded in the surfaces of the LDPE particles during the ball milling procedure, and stay aggregated at the boundaries between LDPE particles during the compression molding at 150°C. The LDPE particles, however, melt and extrude into the inter-particle spaces resulting in high filler concentration composite layers between LDPE core regions where particle concentrations remain low. As this process progresses under the hot press, the resulting structure develops into an inhomogeneous mixture of regions with high and low filler concentrations. At a low filler concentration, the particles do not completely cover the surfaces of the LDPE particles and the LDPE cores join to form a continuous matrix phase leaving ZnO nanoparticles scattered in lumps. As the filler concentration increases, the high volume fraction regions form many paths extending throughout the entire specimen.

The electrical resistivities of disc specimens having different filler concentrations were measured and are shown in Fig. 2. For comparison, the resistivities of specimens with homogeneous micron-size and nano-size filler distributions, reported in Ref. 8, are also shown. The percolation limit decreases as the particle size decreases and even more so as a result of inhomogeneous filler distribution. The slope of the resistivity curve as a function of filler content for the samples with inhomogeneous distribution is close to the slope for composites with homogeneously distributed micron particles. On the other hand, the resistivities for composites with homogeneously distributed nanoparticles exhibit slow decrease in resistivity above the percolation limit but fast decrease followed as the filler concentration increases further. It is thought that the conduction mechanism is different for the two sets of samples as illustrated in Fig. 3. In the composites with homogeneous distribution of filler particles, electrons can tunnel between particles

through thin layers of the insulating matrix and this tunneling occurs throughout the entire specimen. This results in a lower slope. In the composites with inhomogeneous filler distributions, electrons are transported between adjacent touching particles or tunnel over very short inter-particle distances. This mechanism increases the conductivity, but the conduction mainly occurs along the network of highly filled areas between the relatively pure LDPE grains. Therefore, the conduction paths for inhomogeneous composites are more conducting, but limited to smaller spatially limited regions compared to the conduction paths in homogeneously distributed composites for a given concentration. However, the net resistivity of the composite is determined by the combination of these two competing effects. At high enough filler concentration, all the samples exhibit the same sharp drop in resistivity with filler concentration which is indicative of a conduction mechanism through the touching particles

Figure 4 exhibits the nonlinear electrical resistivity of the inhomogeneous nanocomposites as a function of applied electric field strength. The resistivity of the percolated composites decreased as the applied field strength increased. The slope of each curve indicates the degree of nonlinearity in the current-voltage (I-V) relationship. The resistivity of pure LDPE does not show any noticeable change in the field strength range shown in Fig. 4. The nonlinearity in this field strength range is inherited from the ZnO nanoparticles and is shown to increase with ZnO filler concentration. The increase of nonlinearity can be understood from the increased local field around the ZnO nanoparticles. Electric field lines in the composite are distorted by the presence of nanoparticles with a conductivity much higher than that of the insulating matrix. The equipotential lines are pushed away from the particles and the local field around the surface of nanoparticles becomes greater than the average applied field strength due to this field-line distortion. This increased local field effect becomes stronger as the filler particle distribution becomes more inhomogeneous. The strongest local field is felt for particles sitting at the interface between high and low filler concentration regions. The nonlinearity of ZnO is greater under a higher electric field and the composite with inhomogeneous filler distribution exhibits greater nonlinearity due to the increased local field (compared with the average applied field) inside the composite.

Conclusion

It has been shown that the percolation limit for the electrical resistivity of polymer nanocomposites can be controlled by the distribution state of the filler particles as well as the size of the fillers. The mechanism of electrical conduction through the composite also changes with the filler particle distribution. These changes in electrical resistivity suggest the ability to design nanocomposites with tailored electrical properties via the control of microstructure as well as the size of the filler particles. Better control of the filler particle distribution and, hence, the microstructure is expected by using fillers and matrix powders of various sizes.
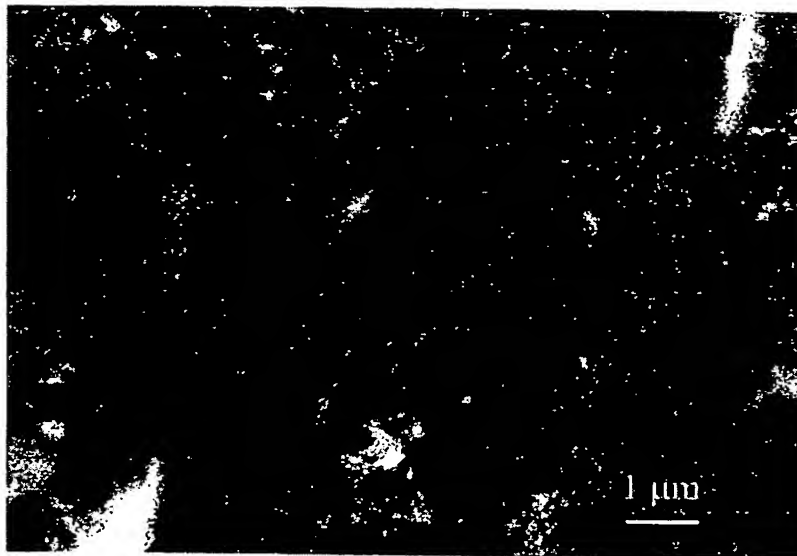
Nonlinear electrical resistivities of LDPE matrix nanocomposites containing ZnO nanoparticle fillers were also affected by the spatial distribution of these nanoparticles inside the composite. Due to the large differences in resistivity between filler and matrix, the electric field distribution around the nanoparticles changes yielding higher local field strengths than the average field strength applied over the thickness of the specimen.

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Figure 1. FESEM micrographs of fracture surfaces from LDPE/ZnO (14 vol. %) nanocomposites with (a) homogeneous filler distribution (reprinted from Ref. 14), and (b) inhomogeneous filler distribution. Nanoparticles appear as white dots in the micrographs.
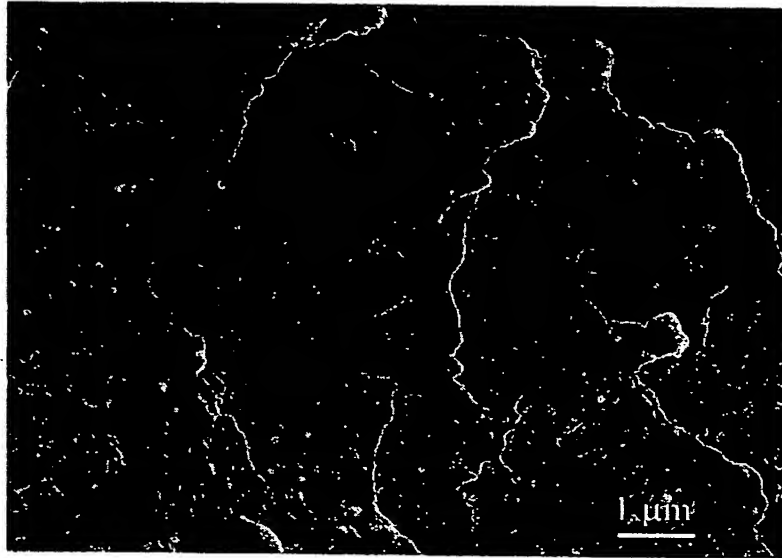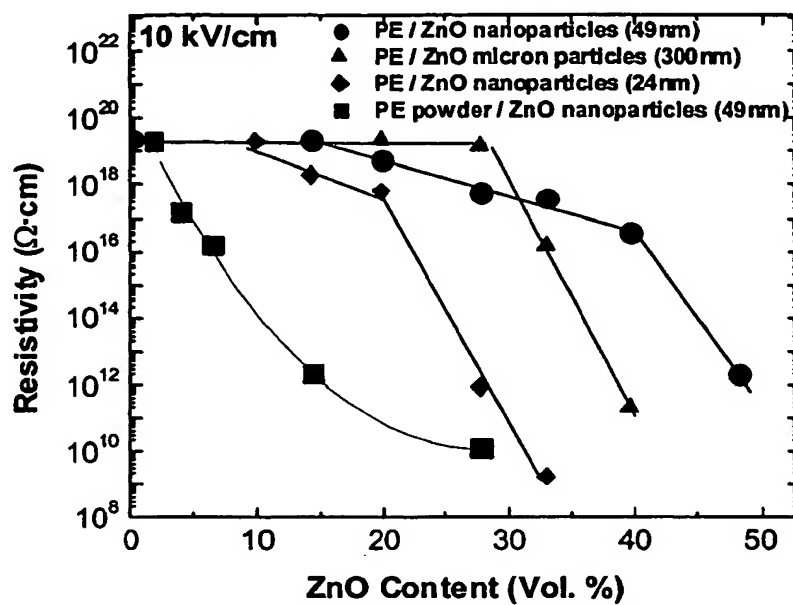

(a)

(b)

Figure 2. Electrical resistivities of LDPE/ZnO composites as a function of ZnO content under an applied field strength of 10 kV/cm. Data for samples with homogeneous (▲, , and ◆) and inhomogeneous (■) filler distribution are shown.
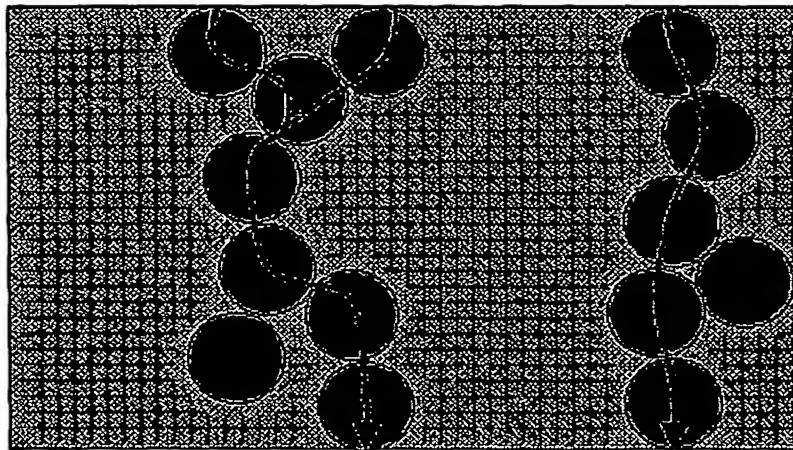

(a)

Figure 3. Schematic illustration of the conduction mechanisms for composites with (a) homogeneous filler distribution, and (b) inhomogeneous filler distribution. Electron conduction is illustrated as arrows.
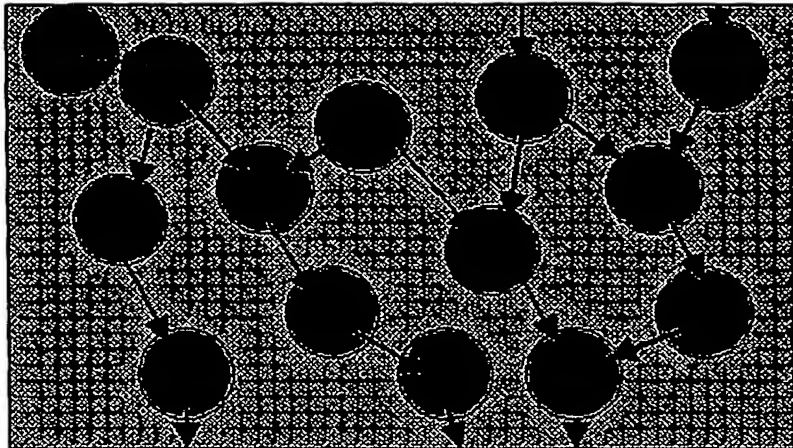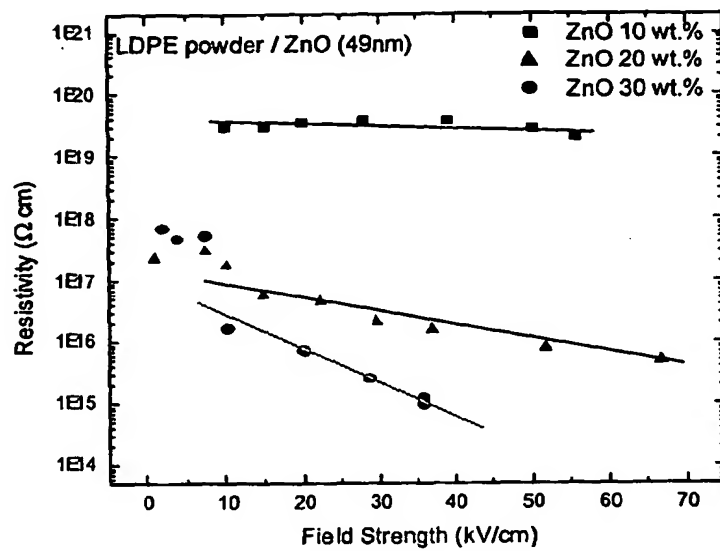

(a)

(b)

Figure 4. Electrical resistivities of ZnO/LDPE inhomogeneous composites (containing 49 nm diameter nanoparticles) as a function of applied field strength.

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Di lectric Prop rti s of ZnO/Low D nsity Polyethylene Nanocomposites

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Abstract

ZnO/low density polyethylene nanocomposites were prepared using melt mixing with good dispersion of the ZnO nanoparticles. The dielectric properties of the composite with various concentrations up to the percolation limit were measured and compared to the electrical properties of conventional sub-micron ZnO filled LDPE.

Introduction

Polymers are used for electrical insulation because of their physical and chemical properties. The high chemical stability of polymers allows their use in harsh conditions, and polymers are generally regarded as good insulating material [1]. Both the mechanical and electrical properties of polymers can be further improved or modified with the addition of inorganic fillers [2]. Increases in the mechanical strength of the composite have been reported [3] and changes of electrical conductivity by additions of carbon black or other conductive fillers [4, 5] have been studied for many years. It is known that the properties can also change with the dispersion state, geometric shape, and surface quality of the filler particles as well as the particle size. For example, Sumita et al. [6] studied the effect of carbon black dispersion in polymer blends on the electrical conduction properties of the composite, and the dependence of electrical properties on the shape and distribution of the filler particles were reported by Flandin et al. [7]

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In recent years, nanoscale fillers have attracted interest because [8] the properties of nanoparticles themselves are different from bulk materials due to their small size and corresponding increase in surface area [9, 10, 11]. It is expected that the addition of nanoparticles into polymers would lead to unprecedented ability to control the electrical properties of filled polymers [12, 13]. This paper provides insight into the mechanisms controlling electrical behavior of nanocomposites using a ZnO/low density polyethylene composite system.

Polyethylene was chosen as a representative polymer matrix in this work because it is one of the most widely used polymers for electrical insulation in the cable and wire industry due to its high breakdown strength and resistivity [14]. Another advantage is that it is relatively easy to mix with inorganic fillers by simple melt-mixing; good dispersion of the filler particles can be readily achieved. ZnO fillers were used since ZnO is a semiconducting material well known for its nonlinear electrical conducting properties, and has been studied by many researchers [15, 16, 17]. By combining the special properties of ZnO nanoparticles [18, 19, 20] with LDPE, a polymeric nanocomposite material with controlled properties could be expected. The conductivity of ZnO is much higher than that of LDPE and is dominated by the properties of its surfaces [20]. The conductivity of the ZnO/LDPE composite is thus expected to change depending on the concentration of ZnO filler as the ZnO inter-particle distance and surface chemistry changes. However, the detailed relationship between the filler concentration and conductivity or permittivity of the composite is still unknown [2]. The behavior near the percolation threshold, p_c (the filler concentration o at which the resistivity starts to change rapidly), is also of interest [21]. Classical percolation theory predicts a power law behavior ($\sigma \approx (p - p_c)^t$) with exponent, t, equal to 2 [21, 22]. However, experimental measurements have frequently reported t values different from 2 [23, 24]. In this paper, we attempt to understand how nanoparticles and their surfaces affect the electrical properties of polymer composites in comparison to those filled with conventional sub-micron size ZnO.

Exp rim ntal

ZnO/LDPE nanocomposites were produced by melt mixing commercial grade DOW 6811 LDPE and 49 nm ZnO nanoparticles in a Haake batch mixer. ZnO nanoparticles were obtained from Nanophase Technologies Corporation. To avoid any thermal degradation of the polymer matrix [25], the mixing time was set to 10 to 13 minutes at 200°C. The specimen was then hot pressed into a disc shape with a diameter of 6.35 cm for the measurements of permittivity.

In order to realize the property changes resulting from the addition of nanoscale fillers, they must be dispersed well within the matrix. To observe dispersion, the composites were cooled below their glass transition temperature and fractured. The fracture surface was examined with field emission scanning electron microscope (JEOL JSM-6335F) operated at 5 kV. As shown in Fig. 1, the particles were dispersed quite well. Nanoparticles are shown as white spheres dispersed throughout the entire area examined.

The permittivity of the nanocomposite was measured using a Quadtech 1689 LCR meter and a home-made electrode fixture with grounded guard ring to minimize the edge effect during the measurements of capacitance.
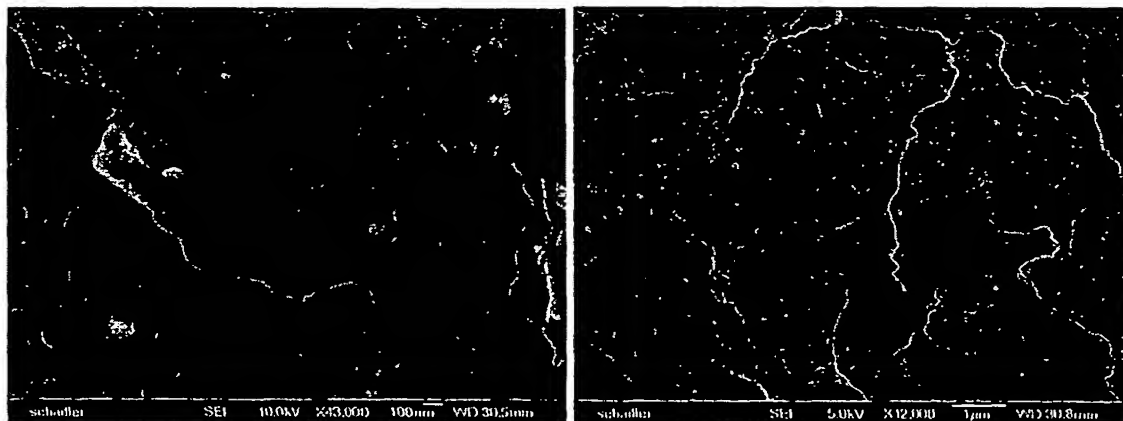

Figure 1. SEM images of the ZnO/LDPE nanocomposite. Good distribution of nanoparticles in the LDPE matrix can be observed.

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Research Note

R sults and Discussions

The permittivity of the nanocomposites were measured to be roughly proportional to the volume content of ZnO particles in the composites, as seen in Fig. 2, following the relationship

$$\varepsilon = \frac{v_m \varepsilon_m (\frac{2}{3} + \frac{\varepsilon_d}{3\varepsilon_m}) + v_d \varepsilon_d}{v_m (\frac{2}{3} + \frac{\varepsilon_d}{3\varepsilon_m}) + v_d}.$$

This relationship was derived by Maxwell for a mixture of spherical particles with dielectric constant ε_d dispersed in a matrix with lower dielectric constant, ε_m, with volume fractions of v_d and v_m, respectively [26]. The trend shown in Fig. 2 is the same for both nanoparticle and micron-particle fillers in spite of the much higher specific surface area of the nanoparticles. Therefore, the interfaces between ZnO filler and LDPE matrix do not make apparent contribution to the permittivity of the composite.

The high surface area of the nanoparticles can be used to introduce extra organic material into the composite by coating the nanoparticle surfaces with silane coupling agents. When such a coating is on the surface of the particles, the permittivity can be increased depending on the dielectric properties of the coating agent. It is demonstrated with composites with filler concentrations of 14 vol. % with various coupling agents as shown in Fig. 2.
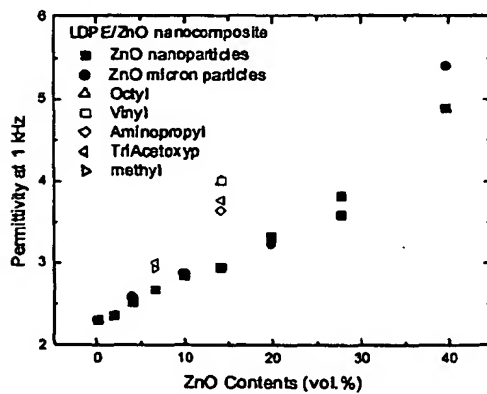

Figure 2. Permittivity of nanocomposites measured at 1 kHz.

The temperature dependences of the permittivity of the composites were also measured by placing the electrode and specimen in a silicone oil bath at elevated temperatures (Fig. 3). Pure polyethylene showed a slight decrease of permittivity as temperature increased. For the composites, the decrease of permittivity at higher temperatures is compensated by the increasing permittivity of the ZnO filler particles with temperature. At about 20 wt.% ZnO, the permittivity remained essentially constant over the temperature range tested, while for the 40 wt.% ZnO samples a measurable increase was observed at higher temperatures. The composites with the higher concentration of ZnO measured (80 wt.%) exhibited a strong increase of permittivity with temperature. The same behavior of increasing permittivity with temperature was observed with LDPE/ZnO micron particle composites.
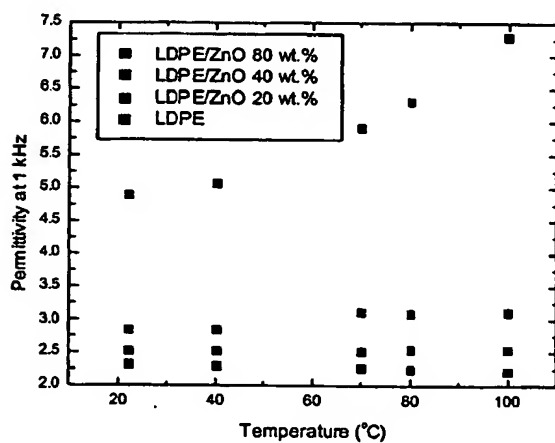

Figure 3 Temperature dependence of permittivity.

Conclusions

The permittivity of the ZnO/LDPE nanocomposites investigated was not affected by the high surface area or small particle size of the nanoparticles used as fillers. The interface between ZnO and LDPE does not appear to contribute to the dielectric properties. On the

other hand, the high surface area of the nanoparticle fillers can be used to introduce surface coating agents with higher permittivity into the composites. The resistivity decreases exponentially with increasing ZnO volume content of the nanoparticles, but at a rate considerably less than expected for a sharp onset of percolation. The electrical conduction seems to be due to the tunneling between ZnO filler particles.

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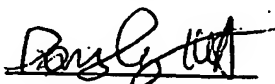[26] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics* (John Wiley and Sons, New York, 1991).

INVENTION DISCLOSURE

The effect of nanoparticle surface chemistry on electrical breakdown of nanocomposites

Polyethylene has played an important role in electrical insulating technology and is one of the most attractive cable insulating materials due to its unique characteristics such as high electrical strength, ease of fabrication, low cost and simple maintenance. Traditionally, micron-size particles have been mixed into polymer matrices to modify the high field stability, high temperature insulating stability, mechanical and thermal–mechanical properties, and resistance to degradation. One property that normally decreases significantly with the addition of filler, however, is the electrical breakdown strength. The most general explanation for this decrease is the local field distortion due to the introduction of micron-size particles. Our results show that by using nanoscale (with diameters less than 100 nm) fillers, there is no loss in breakdown strength and, furthermore, the breakdown strength depends strongly on the surface chemistry of the nanoscale fillers. Here we define the breakdown strength as the electrical failure strength at the cumulative failure probability of 63.2% obtained from a Weibull distribution.

We have found that the introduction of as-received nanoscale TiO_2 or micron-size TiO_2 decreased the breakdown strength by about 40 %. Low-density polyethylene (LDPE) filled by dried nanoscale TiO_2 has a breakdown strength similar to that of unfilled LDPE and are significantly higher than that filled with dried conventional size scale TiO_2. The hydrophilic nature of TiO_2 nanoparticles leads to surface water, which is conductive and causes early breakdown of the overall system. After drying the nanoscale TiO_2 in a vacuum oven at $195^{\circ}C$ for one day, the molecularly adsorbed water was removed. In order to decrease the readsorption of water from atmospheric humidity, surface coatings that change the nanoparticle surface from hydrophilic to hydrophobic are necessary. Our results show that this can be accomplished by attaching hydrophobic groups on the nanoparticle surfaces.

In addition to protecting nanoparticle surfaces from water attack, surface coatings also can improve the interface between the nanoparticles and the polymer matrix, thus influencing electrical breakdown. Because of the large surface area of nanoparticles, the interface region, which is also the electric field concentrated region, plays an important role in the final insulating performance of the composite. The improvement of the interface region can be achieved either by using long chain coupling agents, which entangle with the polymer matrix, or coupling agents having functional groups, which may react with the polymer matrix. A surface coating with tailored functional groups can as well improve the space–charge distribution in the polymer matrix. This would further enhance the high field stability of the insulating material. Our conclusion that the surface chemistry of nanoparticles and the interface between nanoparticles and the polymer matrix influence electrical breakdown significantly can be easily extended to other nanocomposite systems.

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4609048   2003

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Inventi n Disclosure Record:

1.As required under part 2 of the Institute's Intellectual Property Policy approved by the
. Board of Trustees on May 21, 1988, I am enclosing a disclosure of Invention titled:
**The effect of nanoparticle surface chemistry on electrical breakdown of
nanocomposites.**

2. Name of Inventors, Address, and Citizenship
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citizen),
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ABB Group Services Center, Våsterås, Sweden

3. Dates
Invention conceived by inventor(s)
First sketch of invention prepared: July, 2002
First written description prepared: August, 2002
First model or full size device completed
First test or operation of invention
First offer of sale
First sale
First public disclosure

4. The invention was made under one or more of the following circumstances:
In connection with sponsored research project number
b) In connection with any agreement of any type which gives or may give any
party rights whatsoever in the invention
If so, please identify the agreement and, if possible, attach a copy.
c) On my own time as follows:
a) Consulting(describe)
b) Other (describe)
c) Use of Institute time, materials, or facilities
d) In connection with Institute Activities:

This was developed as part of the Rensselaer Nanotechnology Center Industrial
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owned by ABB and RPI (See Chuck Rancourt for details)

5. List names of each person (other than co-inventors) who have knowledge of
the invention.
Jung-IL Hong (RPI)
Thomas Liljenberg (ABB)

Influence of Nanoparticle Surface Water on the Breakdown Strength of Nanoparticle-Filled Low-Density Polyethylene

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Abstract:

The breakdown strength of TiO_2 nanoparticle filled low-density polyethylene (LDPE) nanocomposites was investigated. Micron-size TiO_2 filler was used for comparison. It was found that the surface water on the particles plays a more important role in determining the breakdown strength than the size of particles. The breakdown strength at 63.2% cumulative failure probability E_0 for the composites with dried nano-scale TiO_2 was similar to that of pure LDPE and 50% higher than the samples filled by as-received nano-TiO_2. This increase could be due to a decrease in the local power loss and field distortion for the dry nanoparticles, a better interface, or a morphology change of the matrix. It was also found that surface modification on nano-TiO_2 has a significant influence on the breakdown strength. N- (2-Aminoethyl) 3-Aminopropyl-Trimethoxysilane (N-amino)-
coated TiO_2 filled samples show 40% higher E_0 than that of uncoated TiO_2 filled samples. It could be due to the change of the space charge distribution caused by polar groups in Namino. Surface modification also increases the water resistance of the samples.

Introduction:

Polymers play an important role in electrical insulating technology because of their high electrical strength, ease of fabrication, low cost and simple maintenance [1-3]. Conventionally, additives have been mixed into polymer matrices to improve their resistance to degradation [4], to modify mechanical and thermo–mechanical properties [5], and to improve electrical properties such as high-field stability [6]. One limitation of conventional additives is the negative effect they can have on breakdown strength. In the ideal case, an additive will both modify the property of interest and increase the breakdown strength or at least not degrade it.

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An example of additives that can improve the breakdown strength is azocompounds [7]. Azocompounds consist of a benzene or naphthalene ring to which one or more radicals are connected. A radical is either an electron-acceptor or electron-donor. The increase of the breakdown strength is due to the trapping and the excitation effect of this additive. On the other hand, plasticizers tend to cause a marked reduction of the breakdown strength [8]. This is because the plasticizer increases the free volume of the polymer, thus leading to an increase in the electron mean free path causing early breakdown. Both of these kinds of additives exist in polymer matrices in their molecular state. Once the additive appears as a separate phase (e.g. filler paritlces) in the polymer matrix, local field distortion becomes an important factor, and in most cases such fillers cause a decrease in the breakdown strength of insulating materials [9-11]. A second phase can also influence the breakdown strength via a tortuosity mechanism, i.e., an increase in the path length of the breakdown [12]; or by changing the space charge distribution [13].

Under ac (alternating current) conditions, local field distortion and enhancement is caused by the difference in permittivity between the additive particles and the polymer matrix, while under dc (direct current) conditions, the local field distortion is caused by the difference in conductivity between the additive particles and the polymer. In these cases, the additive particles act as local field enhancing defect centers. When the same kinds of particles, which have the same permittivity or conductivity, are used, the local field distortion is only determined by the size of the particles. The larger the particles are, the larger the field enhancement. Therefore, nanoparticles are expected to result in less of a loss in breakdown strength than traditional fillers. In this paper we explore the effect of particle size and surface area on breakdown strength of polyethylene under DC conditions.

Experimental Approach

The matrix used in this study was low-density polyethylene (LDPE) DOW 681I. The basic characteristics of LDPE 681I are: density 0.922 g/cc and melt index 1.2 g/10 min. Both micron-scale (1-2 µm) from Aldrich and nano-size (23 nm average diameter) TiO_2 from Nanophase were used as fillers. Five weight percent TiO_2 particles were mixed into LDPE at 130^0C in a melt mixer. Films with a thickness of 10-40 µm were obtained using compression molding at 160^0C under a pressure of about 14 MPa. The temperature of the film was decreased to 50-60^0C slowly in the mold under pressure before it was removed from the mold and air-cooled to room temperature. Each sample was then kept in a desiccator for at least one day before the breakdown strength was measured in case residual internal stress influences the experimental results. Unfilled pure LDPE went through exactly the same process in order to reduce the effects of processing on the results. TiO_2 particles with three different surface conditions were used: as received, vacuum dried at 195^0C for 24 hrs, and surface modified.

The surface modification was carried out by toluene reflux. Both N- (2-Aminoethyl) 3-Aminopropyl-Trimethoxysilane (N-amino) and Decyltrichlorosilane(Decyl)

from Gelest. Inc. were used as coupling agents. Toulene was first dried by CaH_2 powder in N_2 atmosphere and purified by distillation. Ten grams of dried nano-TiO_2 were dispersed by sonication at 70% power for 5 minutes in dried toluene. Coupling agent was slowly added to the nano-TiO_2 / toluene mixture. Then the mixture was put into oil bath at 135 ^0C and magnetically stirred for 24 hrs. The resulting slurry was centrifuged at 6,000 rpm for 10 minutes, and then washed twice with toluene. Finally, the modified particles were dried in a vacuum oven at about 30 °C for 24 hrs.

A sphere-plane setup was used for the breakdown measurements. The diameter of the sphere was ¼ inch (0.635 cm). The spherical electrode was connected to a high potential, while the plane electrode was connected to ground potential. The test was performed at room temperature using a stepwise voltage. Each voltage step was 100V and was maintained for approximate 1 second before the high voltage electrode was grounded and the next higher voltage was applied. The process proceeded until breakdown occurred showing a sharp current increase. Breakdown strength is defined as the electrical voltage divided by the sample thickness.

Water absorption was checked by immersing samples into water at 50 °C oil bath and measuring the weight change.

A Weibull distribution was used to analyze the breakdown data. This distribution has been found to be the most appropriate for breakdown analyses [10, 14]. The cumulative probability of the electrical failure takes the form of

$$P\,(E) = 1\text{-exp}\left[-\left(\frac{E}{E_0}\right)\right]^{\beta} \qquad \text{(1) Change } E_0$$

Where β is a shape parameter, and E_0 is a scale parameter that represents the breakdown strength at the cumulative failure probability of 0.632. We will use E_0 to show the significance in the differences between several sets of breakdown data.

Results

Breakdown strength is defined as the electric field intensity that causes an "insulator-to-conductor" transition in a material and is accompanied by a sharp increase in current. Fig.1 shows the Weibull plots of the breakdown strength of pure LDPE samples and of the samples containing as-received nano-TiO_2, dried nano-TiO_2 or dried micro-TiO_2 particles.

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The difference in E_0 obtained from the linear regression of the Weibull plot for these four kinds of samples is clearly shown in Fig.2. The results are also summarized in Table 1.

With the incorporation of 5 wt% as-received nano-scale TiO_2, a 40% decrease in the breakdown strength was observed as compared to pure LDPE which has an E_0 of 3.78MV/cm. A 95% confidence interval (not shown here) indicates that this difference is significant. The breakdown strength, E_0, of of dried nano-scale TiO_2 / LDEP is 3.51MV/cm, close to that of pure LDPE. Due to a partial overlap of the 95% confidence bounds, the breakdown strength of the samples containing dried nano-scale TiO_2 is not significantly different from that of unfilled LDPE. However, the difference in breakdown strength between the as received and dried nanoscale titania / LDPE composites is significant indicating that drying the nanoparticle surface has a significant effect on the breakdown strength.

This conclusion was further verified by comparing the E_0 of the samples filled by the as-received nano-scale TiO_2 and E_0 of those filled by the dried micro-TiO_2. The latter show higher breakdown strength although the average size of the additive particles in the latter is 40~90 times larger than that of the additive particles in the former. This indicates that the water absorption on the surface of the nanofillers has a much larger effect on breakdown strength than particle size.

The surface of oxide nanoparticles is always covered by hydroxyl groups (M-OH) and physically adsorbed water hydrogen bonded to the surface hydroxyls. Thermogravimetry (TGA) was used to investigate the oxide surface before and after the drying treatment. It was found (Figure 3) that the drying process at 195^0C efficiently removed the surface water as shown by the lack of weight loss below 300^0C after drying. After drying there is weight loss above 300^0C indicating that there are still hydroxyl groups on the surface [15]. If we assume the difference in weight loss at 300^0C is due to the total removal of the physically adsorbed water layer on the

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nanoparticle surface, then the surface water accounts for about 0.93 wt % in as-received nano-scale TiO_2. When 5 wt% as-received nanoparticles were put into the polymer matrix, the overall water content goes down to as low as 0.047 wt%. It is worthwhile to pursue how such a small amount of water has such a significant effect on the breakdown strength. The possible reasons are presented. First, the conductive water layer on the nano-scale TiO_2 surface causes conductive power loss. This may result in an increase of temperature locally, causing burning and decomposition of the surrounding polymers. Thus, thermal breakdown occurs. In addition, the conductive water layer may further increase the local field distortion by changing the space charge distribution. This could lead to breakdown across the interface. In addition to removing water, drying the interface leads to a better interface because the surface is less hydrophilic as observed by the ease with which the dried particles float on water while the wet ones sink. Finally, morphology changes may contribute to the increase of the breakdown strength of dried nano-scale TiO_2 filled samples. It is quite possible that nano-scale TiO_2 acts as a nucleation site and promotes heterogeneous nucleation of LDPE. The surface tension of the nucleation centers is one of the factors determining lamellar thickness. The existence of the water causes the different surface energy, thus different lamellar thickness, and accordingly that may influence the breakdown strength. More supplementary work needs to be done to fully understand the mechanism.

Fig.4 shows water absorption of unfilled LDPE, dried nano-scale TiO_2 filled LDPE and Decyl-coated nano-scale TiO_2 filled LDPE. Water gets saturated in pure LDPE just after a couple of days, but for dried nano-scale TiO_2 filled LDPE, the water absorption is continuing even after 17 days. This can be easily understood. Evidently, water absorption is enhanced by putting quite a few hydrophilic nanoparticles into the hydrophobic matrix. Because of the

possibility that water could readsorb onto the particles with time and decrease the breakdown strength, Decyl, which is hydrophobic, was used to coat nano-scale TiO_2 surface to increase its water resistance. It can be seen in Fig.4 that the water absorption decreased as a result of the surface modification.

Fig.5 compares E_0 of unfilled PE, as-received nano-scale TiO_2 filled LDPE, and Namino-coated nano-scale TiO_2 filled PE.

Although after surface modification, E_0 is still lower than unfilled LDPE, it is about 40% higher than uncoated nano-scale TiO_2 filled PE. It again indicates that the surface chemistry has an important influence on E_0. It is quite possibly due to either an increase in electron scattering or a change in the space change distribution in the samples because of the existence of polar groups in Namino. The result is promising. We can expect that by choosing a very "good" coupling agent, E_0 obtained can be even higher than that of pure LDPE.

To fully characterize the breakdown strength, not only E_0, but also the spread of the data has to be considered. According to [14], the shape parameter β determined by the linear regression method represents the spread of breakdown strength: β tends to decrease with an increase in scatter. Our results show the same trend by comparing β with the standard deviation shown in Table1. Note that except for the dried nano-scale TiO_2 filled samples, the data for composites filled by with as-received nano-scale TiO_2, the dried micron-TiO_2, or Namino-coated nano-scale TiO_2 show much lower scatter than that of unfilled LDPE. A similar phenomenon has been reported by M.M.Veki and M.Zanin [14].

In summary, surface chemistry such as the existence of surface water and surface silane has a much more significant influence than the size of the nanoparticles on the breakdown strength. By using the dried nano-scale TiO_2, E_0, the breakdown strength at the cumulative failure

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probability of 63.2% was increased by 50% compared with the samples filled by the as-received nano-scale TiO_2, close to that of unfilled LDPE. Namino-coated nano-scale TiO_2 filled samples show a 40% increase in E_0 compared with that of uncoated nano-scale TiO_2 filled samples. Further work needs to be done for a full understanding of the effect of surface chemistry of fillers on the breakdown strength.

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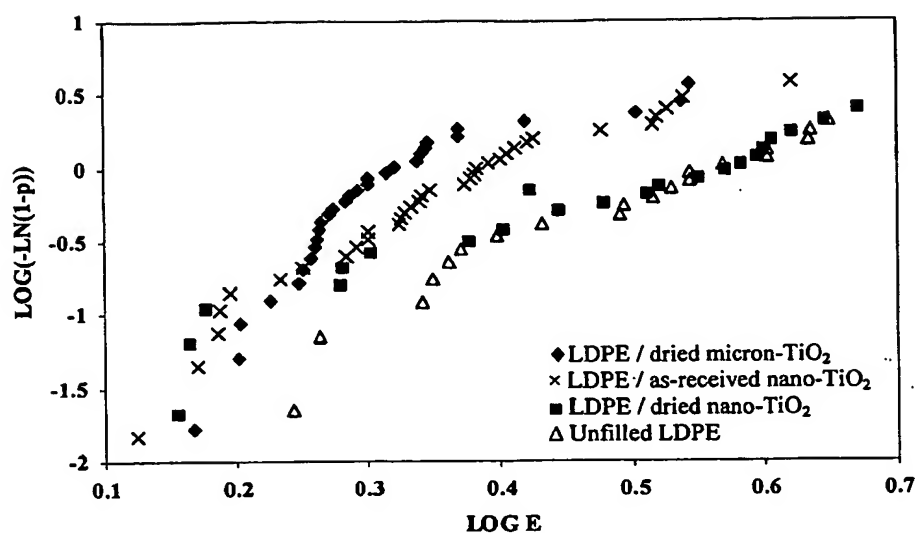[15]M.Primet, P.Pichat, and M.V.Mathieu, *The journal of Physical Chemistry*, 75, 1216 (1971).

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Fig.1 Linear regression of the Weibull distribution.
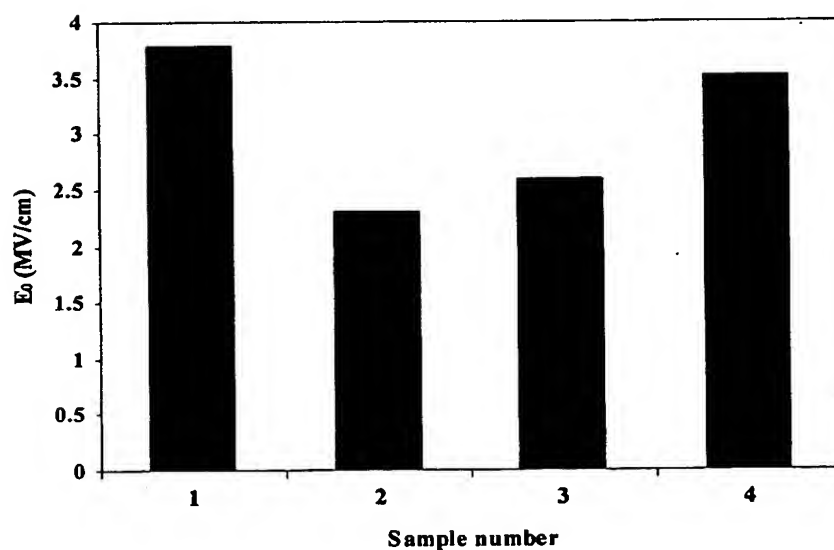
Fig.2 E_0 determined by linear regression for (1) unfilled LDPE, (2) LDPE / as-received nano-scale TiO_2, (3) LDPE / dried micro-TiO_2, and (4) LDPE / dried nano-scale TiO_2.

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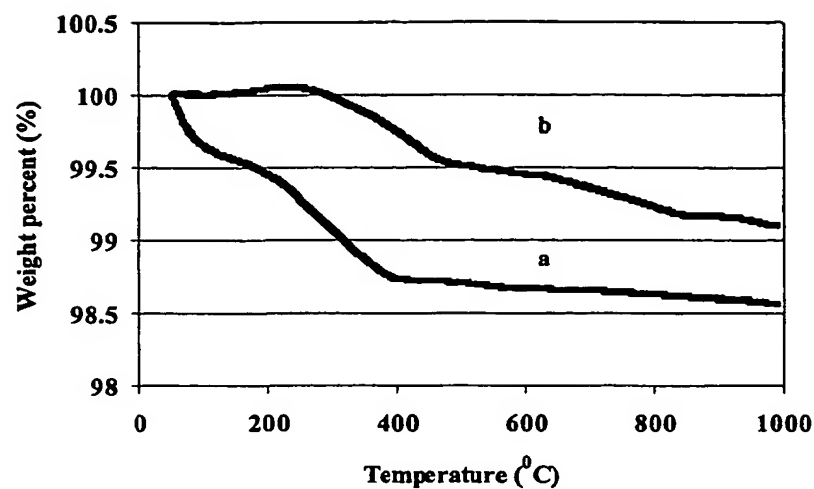
Fig. 3 Weight loss of nano-scale TiO_2 (a) before and (b) after drying treatment.

Table 1 Comparison of the breakdown strength and the scattering of data.

Sample	Average BD (MV/cm)	Standard Error (MV/cm)	E_0 (MV/cm)	β	Data amount
Unfilled LDPE	3.37	1.14	3.78	3.53	22
LDPE / as-received nano-scale TiO_2	2.10	0.50	2.30	5.12	30
LDPE / dried Micron-TiO_2	2.41	0.64	2.58	4.51	34
LDPE / dried nano-scale TiO_2	3.12	1.13	3.51	3.03	23
LDPE / Namino caoted nano-scale TiO_2	2.75	0.78	3.13	3.31	24

Note: BD-Breakdown strength

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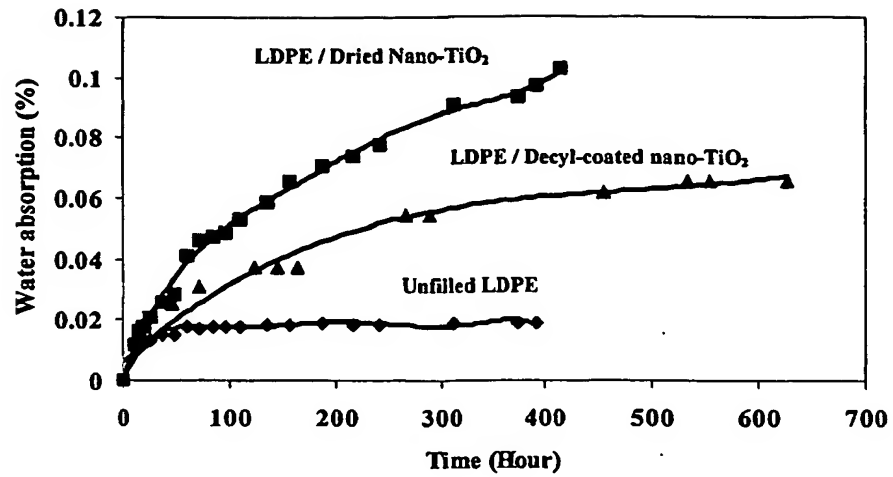
Fig.4 The comparison of water absorption.
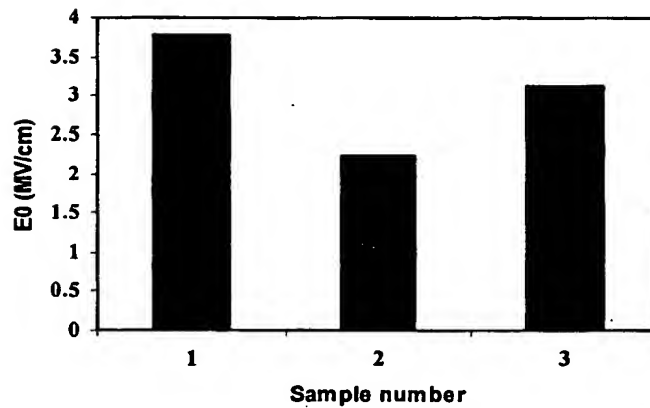
Fig.5 E_0 determined by linear regression for (1) unfilled LDPE, (2) LDPE / as-received nano-scale TiO_2, (3) LDPE / Namino-TiO_2.

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